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CLAIMS

[Claim(s)]

[Claim 1] (A) The positive type radiation-sensitive resin constituent containing the component and the (D) organic solvent which generate an acid by the exposure of the polymer which has the acid dissociation nature functional group which dissociates with an acid and produces an acid functional group, (B) Pori (vinyl low-grade alkyl ether), and the (C) radiation.

[Claim 2] (A) When the sum total of the polymer and (B) Pori (vinyl low-grade alkyl ether) which have the acid dissociation nature functional group which dissociates with an acid and produces an acid functional group is made into the 100 weight sections (B) Positive type radiation-sensitive resin constituent according to claim 1 whose content of the (D) organic solvent the content of the component for which the content of Pori (vinyl low-grade alkyl ether) generates an acid by the exposure of 5 - 60 weight section and the (C) radiation is the 20 - 400 weight section at 0.1 - 20 weight section and a list.

[Claim 3] (B) The positive type radiation-sensitive resin constituent according to claim 1 or 2 whose polystyrene equivalent weight mean molecular weights of Pori (vinyl low-grade alkyl ether) are 1,000-200,000.

[Claim 4] (A) A positive type radiation-sensitive resin constituent given in any of claims 1-3 characterized by the boiling point in one atmospheric pressure of the acid dissociation matter which this acid dissociation nature functional group in the polymer which has the acid dissociation nature functional group which dissociates with an acid and produces an acid functional group dissociates, and is generated being 20 degrees C or more they are.

[Claim 5] (b) A positive type radiation-sensitive resin constituent given in any of claims 1-4 they are The process which dries after applying on the substrate which has a conductive layer on a front face, and forms the resin film, The process which carries out exposure afterbaking of the radiation to the (b) this resin film at a predetermined configuration, develops negatives further, and forms a pattern, The process which uses as mold this pattern formed on the substrate, carries out electrolytic plating to predetermined thickness, and forms a plating molding object, (Ha) The manufacture approach of the plating molding object characterized by coming to pass the process which exfoliates a resin film part from a (d) substrate, and the process which removes conductive layers other than the field in which the plating molding object on a (e) substrate was formed.

[Claim 6] Positive type radiation-sensitive resin film which it comes to form by exfoliating this base material film after applying a positive type radiation-sensitive resin constituent given in any of claims 1-4 they are on a base material film and drying.

[Claim 7] (b) The process which carries out the laminating of the positive type radiation-sensitive resin film according to claim 6 on the substrate which has a conductive layer on a front face, The process which carries out exposure afterbaking of the radiation to the resin film by which the (b) laminating was carried out at a predetermined configuration, develops negatives further, and forms a pattern, The process which uses as mold this pattern formed on the substrate, carries out electrolytic plating to predetermined thickness, and forms a plating molding object, (Ha) The manufacture approach of the plating molding object characterized by coming to pass the process which exfoliates a resin film part from a (d) substrate, and the process which removes conductive layers other than the field in which the plating molding object on a (e) substrate was formed.

[Claim 8] The manufacture approach of the plating molding object of claim 5 or claim 7 characterized by the thickness of formation or the resin film by which the laminating was carried out being 20-100 micrometers on a substrate.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is concerned with the manufacture approach of a positive type radiation-sensitive resin constituent and a plating molding object, and is concerned with the manufacture approach of a plating molding object suitable as the bump at the time of mounting in an integrated circuit device who uses the positive type radiation-sensitive resin constituent concerned for the positive type radiation-sensitive resin constituent which contains in more detail the polymer and Pori (vinyl low-grade alkyl ether) which have an acid dissociation nature functional group as a resinous principle, and a list, or wiring.

[0002]

[Description of the Prior Art] Multi-pin thin film mounting for the shift to the integrated circuit fitted to the specified use called high integration and ASIC of a large-scale integrated circuit (LSI) progressing rapidly with detailed-izing of an integrated circuit device, therefore carrying LSI in electronic equipment in recent years is needed and *(ed), and bare chip mounting by the tape automation TEDDO bonding (TAB) method or the flip chip method etc. has been adopted. By such multi-pin thin film mounting method, it is required to arrange a projection electrode with a height of 10 micrometers or more called a bump with high precision on a substrate as a terminal for connection, and a bump's highly precise-ization will be further needed from now on corresponding to the further high integration of LSI. This bump is processed in current and the following procedures. That is, on the wafer into which the LSI component was processed, the laminating of the barrier metal used as a conductive layer is carried out, and an admiration radioactivity resin constituent and the so-called resist are applied, and it dries. Subsequently, after irradiating a radiation through a mask so that the part which forms a bump may carry out opening (henceforth "exposure"), negatives are developed, and a pattern is formed. Then, electrode materials, such as gold and copper, are deposited by electrolytic plating by using this pattern as mold. Subsequently, after exfoliating a resin part, etching removes barrier metal. Then, a chip is cut down by the rectangle from a wafer and it moves to mounting processes, such as packaging, such as TAB, and a flip chip.

[0003] In a series of processing processes of a bump mentioned above, the following properties are demanded from the resist.

- A paint film with a uniform thickness of 20 micrometers or more can be formed.
- Since it corresponds to a bump's ** pitch-ization, definition is high.
- Near and a pattern have the side attachment wall of the pattern used as mold perpendicularly faithful to a mask dimension.
- In order to raise the productive efficiency of a process, development nature is good at high sensitivity.
- Have the good wettability to plating liquid.
- At the time of plating, a resist component is eluted in plating liquid and don't degrade plating liquid.
- Have high adhesion to a substrate so that plating liquid does not ooze out to the interface of a substrate and a resist at the time of plating.
- It has sufficient reinforcement which can resist the growth stress of plating, and the configuration of the pattern used as mold is imprinted faithfully, and a plating molding object faithful to a mask dimension can be formed.
- When you rinse a substrate and you dry during plating and after plating, a crack should not occur in a paint film.
- After plating should exfoliate easily with exfoliation liquid.

[0004] Although the negative-mold radiation-sensitive resin constituent (refer to JP,10-207067,A) which uses novolak resin and a naphthoquinonediazide radical content compound as a principal component was conventionally used as a resist for bump processing, the pattern configuration became forward tapered shape-like, the pattern which has a perpendicular side attachment wall was not obtained, and since sensibility was low, the exposure time became long, and this resist had the trouble that productive efficiency was low. And this resist has the inadequate reinforcement to the growth stress of plating, and the problem of being easy to generate a crack is in the pattern formed from the resist, and it was not able to say that it was still more enough also in respect of the fidelity over resolution and the mask dimension of the plating sludge of a thick film. Moreover, it is known by blending Pori (vinyl low-grade alkyl ether) with the resist containing novolak resin, a polyvinyl phenol, and an azide compound or a diazo compound that flexibility can be given to a paint film (refer to JP,63-63892,B and JP,60-12621,B). However, it cannot be satisfied with fields, such as fidelity over a pattern configuration, sensibility, resolution, and the mask dimension of the plating sludge of a thick film, of these resists as well as the resist of said JP,10-207067,A.

[0005] Many positives resist of the chemistry magnification mold of the high sensitivity and high resolution containing the resin which has the acid dissociation nature functional group which dissociates with an acid and produces an acid functional group as a resist for thin films on the other hand, and the component which generates an acid by the exposure of a radiation are known. However, when it was going to form the plating molding object from these chemistry magnification types of positive resist, and a substrate is rinsed and it dries after plating in plating liquid, the problem that a crack occurs is in a resist pattern by the environmental variations (for example, change of temperature, change of dryness, etc.) on which are recording of the internal stress by the growth stress of plating and a resist pattern are put. And if a crack arises in the resist pattern under plating, plating liquid will ooze out and it will lead to deformation of a plating sludge. Moreover, if a crack arises in the resist pattern after plating, even if it becomes clear that plating thickness runs short by inspection, it cannot re-plate but a terrible blow will be suffered in respect of economical efficiency and productivity. On the other hand, although generating of a crack mentioned above by lower the molecular weight of the base resin use for the positive resist of a chemistry magnification mold, or lower a glass transition point can be prevent, in plating liquid with the large growth stress of plating, or under plating [that plating temperature exceed 65 degrees C] conditions, a resist pattern become soft or swell shortly, and the problem that where of the configuration of a plating sludge shift from a predetermined configuration greatly be generate.

[0006]

[Problem(s) to be Solved by the Invention] This invention is made as a result of examining wholeheartedly the constituent of the radiation-sensitive resin constituent used as resists for processing, such as a bump, in view of said trouble in the conventional technique. Especially the technical problem does not produce a crack in a resist pattern by rinsing and desiccation under plating and after plating. The manufacture approach of the positive type radiation-sensitive resin constituent which could form the plating molding object of thick films, such as a bump or wiring, with a sufficient precision, and was excellent in sensibility, resolution, etc., and the plating molding object which uses the positive type radiation-sensitive resin constituent concerned for a list is offered.

[0007]

[Means for Solving the Problem] According to this invention, said technical problem is attained more by the positive type radiation-sensitive resin constituent containing the component and the (D) organic solvent which generate an acid by the exposure of the polymer which has the acid dissociation nature functional group which dissociates with the (A) acid in the first place, and produces an acid functional group in the first place, (B) Pori (vinyl low-grade alkyl ether), and the (C) radiation.

[0008] According to this invention, said technical problem to the second the (b) aforementioned positive type radiation-sensitive resin constituent The process which dries after applying on the substrate which has a conductive layer on a front face, and forms the resin film, The process which carries out exposure afterbaking to the (b) this resin film at a predetermined configuration, develops negatives further, and forms a pattern, The process which uses as mold this pattern formed on the substrate, carries out electrolytic plating to predetermined thickness, and forms a plating molding object, (Ha) It is attained more by the manufacture approach of the plating molding object characterized by coming to pass the process which exfoliates a resin film part from a (d) substrate, and the process which removes conductive layers other than the field in which the plating molding object on a (e) substrate was formed.

[0009] According to this invention, after said technical problem applies said positive type radiation-sensitive resin constituent to the third on a base material film and dries, it is attained more by the positive type radiation-sensitive resin

film which it comes to form by exfoliating this base material film.

[0010] According to this invention, said technical problem to the fourth the (b) aforementioned positive type radiation-sensitive resin film Exposure afterbaking is carried out to the process which carries out a laminating on the substrate which has a conductive layer on a front face, and the resin film by which the (b) laminating was carried out at a predetermined configuration. The process which furthermore develops negatives and forms a pattern, the process which uses as mold this pattern formed on the substrate (Ha), carries out electrolytic plating to predetermined thickness, and forms a plating molding object, It is attained more by the manufacture approach of the plating molding object characterized by coming to pass the process which exfoliates a resin film part from a (d) substrate, and the process which removes conductive layers other than the field in which the plating molding object on a (e) substrate was formed.

[0011] An acid generates the positive type radiation-sensitive resin constituent of this invention by exposing for the component (henceforth a "radiation-sensitive acid generator") which generates an acid by exposure contained in it. By the catalysis of this acid When chemical reactions (for example, a polar change, decomposition of a chemical bond, crosslinking reaction, etc.) occur in the resin film (namely, resist coat) which consists of the positive type radiation-sensitive resin constituent concerned, the solubility over a developer forms a pattern using the phenomenon of changing in the exposure section. It is as follows when the molding machine style of this pattern is explained further. By the catalysis of the acid generated by exposure to a radiation-sensitive acid generator, this acid dissociation nature functional group in the polymer which has the acid dissociation nature functional group contained in a positive type radiation-sensitive resin constituent dissociates, an acid functional group is produced, and, as a result, the solubility over the alkali developer of a polymer increases in the exposure section. Moreover, dissociation of this acid dissociation nature functional group is promoted by heating after exposure (it being called "PEB" Post Exposure Bake and the following.). The newly generated acid will exert a catalysis on the next dissociation, and dissociation of an acid dissociation nature functional group and generating of an acid "will be amplified" by dissociation of this acid dissociation nature functional group one after another. A predetermined pattern is formed in high sensitivity (namely, low light exposure) and high resolution by using such a chemistry magnification operation.

[0012]

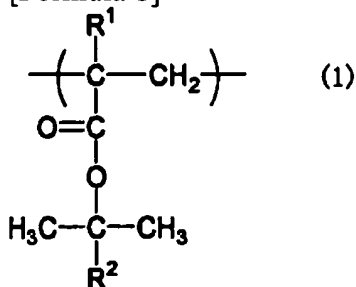
[Embodiment of the Invention] Hereafter, this invention is explained concretely.

As a polymer (henceforth "a polymer (A)") which has the acid dissociation nature functional group which dissociates with the acid used for polymer (A) this invention, and produces an acid functional group The radical polymerization nature monomer which has said acid dissociation nature functional group although it is not limited especially as long as it has the acid dissociation nature functional group which dissociates with an acid, for example, generates acid functional groups, such as a carboxyl group and a phenolic hydroxyl group, (it is hereafter called "a monomer (I)".) The repeating unit to which the polymerization nature unsaturated bond cleft (it is hereafter called an "acid dissociation nature repeating unit".) The polymer to contain is desirable.

[0013] As a repeating unit which dissociates with an acid among acid dissociation nature repeating units, and generates a carboxyl group For example, t-butyl (meta) acrylate, tetrahydropyranyl (meta) acrylate, 2-t-butoxy carbonylmethyl (meta) acrylate, 2-benzyloxy carbonylethyl (meta) acrylate, 2-methyl adamantyl (meta) acrylate, 1, and 1-dimethyl-3-oxo-butyl (meta) acrylate, The unit in which the polymerization nature unsaturated bond of t-butoxy cull BONIRUMETOKISHI styrene cleft, and the repeating unit expressed with the following general formula (1) (it is hereafter called "a repeating unit (1)".) etc. -- it can mention.

[0014]

[Formula 1]



In [general formula (1), R1 shows a hydrogen atom or a methyl group, and R2 shows the univalent alicycle group machine of the carbon numbers 6-20 which may be permuted, or the univalent aromatic series radical of carbon numbers 6-20 which may be permuted.]

[0015] It sets to a general formula (1) and is R2. As a univalent alicycle group machine of the carbon numbers 6-20 which may be permuted, a cyclohexyl radical, a cycloheptyl radical, a cyclo octyl radical, 2-methylcyclohexyl radical, 3-methylcyclohexyl radical, 4-methylcyclohexyl radical, a 4-chlorocyclohexyl group, a 4-t-butyl cyclohexyl radical, a norbornyl radical, an isobornyl radical, an adamantyl radical, 2-methyl adamantyl radical, a tricyclo deca nil radical, etc. can be mentioned, for example.

[0016] Moreover, R2 As a univalent aromatic series radical of the carbon numbers 6-20 which may be permuted, a phenyl group, o-tolyl group, m-tolyl group, p-tolyl group, 4-chlorophenyl radical, a 4-t-buthylphenyl radical, 1-naphthyl group, benzyl, etc. can be mentioned, for example.

[0017] Furthermore, the unit in which polymerization nature unsaturated bonds, such as hydroxystyrene protected by acetal radicals, such as p-1-methoxyethoxy styrene and p-1-ethoxy ethoxy styrene, and t-butoxy styrene, t-butoxycarbonyloxy styrene, cleft as a repeating unit which dissociates with an acid and generates a phenolic hydroxyl group, for example can be mentioned.

[0018] In the case of the repeating unit to which this dissociation generates the acid dissociation matter, for example, a repeating unit (1) originates in 2-benzyl propyl (meta) acrylate, a polymer (A) generates 2-benzyl propene while the acid dissociation nature functional group in that acid dissociation nature repeating unit dissociates with an acid and generates an acid functional group. When the boiling point (only henceforth the "boiling point") in one atmospheric pressure of this acid dissociation matter is below a room temperature, there is a possibility of having a bad influence on the pattern configuration at the time of manufacturing a plating molding object. Generally, when it is about 1-2 micrometers like [in case the thickness of a resist coat forms the circuit of an integrated circuit device], even if it is the acid dissociation matter with which the boiling point is less than 20 degrees C, the inside of a resist coat is penetrated as gas constituents in process of PEB, and a pattern configuration is not affected in practice. However, with the resist coat for manufacturing a bump etc., when the gas constituents which may have to make thickness thick to 20 micrometers or more, and were generated pile up in a resist coat and formed and develop big air bubbles, there is a possibility that a pattern configuration may be spoiled remarkably. For this reason, when the acid dissociation matter is a low-boiling point and the boiling point is less than 20 degrees C, use is difficult for an application by which the thickness of a resist coat exceeds 20 micrometers.

[0019] therefore, as an acid dissociation nature repeating unit in a polymer (A) On the unit and twist concrete target whose boiling point of the acid dissociation matter generated is 20 degrees C or more The repeating unit to which the polymerization nature unsaturated bond of 1 and 1-dimethyl-3-oxo-butyl (meta) acrylate cleft, A repeating unit (1) etc. is still more desirable and the repeating unit to which the polymerization nature unsaturated bond of 1 and 1-dimethyl-3-oxo-butyl (meta) acrylate or 2-benzyl propyl (meta) acrylate cleft especially is desirable. The boiling point of the acid dissociation matter generated from a 1 in polymer (A) and 1-dimethyl-3-oxo-butyl (meta) acrylate unit is about 130 degrees C in 4-methyl-4-pentene-2-ON, and the boiling point of 2-benzyl propene is about 170 degrees C. In a polymer (A), an acid dissociation nature repeating unit can be independent, or can exist combining two or more sorts.

[0020] a polymer (A) can contain the repeating unit (the following -- "-- others -- it is called repeating unit".) to which polymerization nature unsaturated bonds of a copolymerizable radical polymerization nature monomer (henceforth "a monomer (II)") other than a monomer (I) cleft further. Monomer (II) If it carries out, for example o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, p-isopropenyl phenol, styrene, Aromatic series vinyl compound; N-vinyl pyrrolidone, such as alpha methyl styrene, p-methyl styrene, and p-methoxy styrene, Hetero atom content alicyclic vinyl compounds, such as N-vinyl caprolactam; Acrylonitrile, Cyano group content vinyl compounds, such as a methacrylonitrile; A 1.3-butadiene, Conjugation diolefins, such as an isoprene; Amide group content vinyl compound; acrylic acids, such as acrylamide and methacrylamide, Carboxyl group content vinyl compounds, such as a methacrylic acid; Methyl (meta) acrylate, Ethyl (meta) acrylate, n-propyl (meta) acrylate, n-butyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, polyethylene-glycol monochrome (meta) acrylate, Polypropylene-glycol monochrome (meta) acrylate, glycerol monochrome (meta) acrylate, Acrylic ester (meta), such as phenyl (meta) acrylate, benzyl (meta) acrylate, cyclohexyl (meta) acrylate, isobornyl (meta) acrylate, and tricyclo deca nil (meta) acrylate, can be mentioned.

[0021] These monomers (II) p-hydroxystyrene, p-isopropenyl phenol, styrene, an acrylic acid, a methacrylic acid,

methyl (meta) acrylate, ethyl (meta) acrylate, n-butyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, benzyl (meta) acrylate, isobornyl (meta) acrylate, etc. are desirable inside. Monomer (II) It is independent, or two or more sorts can be mixed and used.

[0022] although it is not what will be limited especially if the ratio of the acid dissociation nature repeating unit in a polymer (A) and other repeating units is range which does not spoil the expected effectiveness of this invention -- a repeating unit (weight ratio) besides acid dissociation nature repeating unit/-- usually -- 5 / 95 - 100/0 -- desirable -- 10 / 90 - 90/10 -- it is 20 / 80 - 80/20 still more preferably. In this case, there is a possibility that the rate of an acid functional group that the content of an acid dissociation nature repeating unit is generated at less than 5 % of the weight may become low, the solubility over the alkaline developer of the polymer obtained may fall, and pattern formation may become difficult.

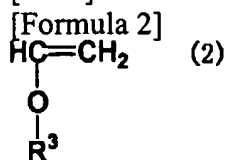
[0023] a polymer (A) -- for example, (i) a monomer (I) -- desirable -- monomer (II) How to carry out direct polymerization (ii) A monomer (I) and p-acetoxy styrene by the case with a monomer (II) How to hydrolyze under basic conditions and to change the acetoxy radical in a polymer into hydroxyl after copolymerizing, (iii) After carrying out the polymerization of the p-t-butoxy styrene, it hydrolyzes under acid conditions. It can denaturalize to Pori (p-hydroxystyrene) and can manufacture by the approach of protecting the hydroxyl in Pori (p-hydroxystyrene) by t-butoxycarbonyloxy radical, a 1-ethoxy ethoxy radical, etc. partially at least after that etc. Although the usual radical polymerization initiator can be used for the polymerization in the approach of the above (i) - (iii) and it can carry it out with proper polymerization methods, such as an emulsion-polymerization method, a suspension-polymerization method, a solution polymerization method, and a bulk-polymerization method, especially its solution polymerization method is desirable.

[0024] As said radical polymerization initiator, organic peroxide, such as azo compounds, such as - azobisisobutyronitril (azobisuisobutironitoriru), and 2 and 2 '2, 2'-azobis - (2,4-dimethylvaleronitrile), and benzoyl peroxide, lauryl peroxide, t-butyl peroxide, etc. can be mentioned, for example. moreover, as a solvent used for said solution polymerization method It is not what will be limited especially if it does not react with the monomer component used but the polymer to generate is dissolved. For example, a methanol, ethanol, n-hexane, toluene, a tetrahydrofuran, 1,4-dioxane, ethyl acetate, n-butyl acetate, an acetone, a methyl ethyl ketone, Methyl isobutyl ketone, 2-heptanone, a cyclohexanone, ethylene glycol monomethyl ether, Propylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, 3-methoxy methyl propionate, 3-ethoxy ethyl propionate, ethyl lactate, gamma-butyrolactone, etc. can be mentioned. These solvents are independent, or two or more sorts can be mixed and used for them. In addition, when a polymer (A) is manufactured by the solution polymerization method, preparation of a positive type radiation-sensitive resin constituent may be presented with the polymer solution obtained as it is, or a polymer (A) may be separated from a polymer solution and preparation of a positive type radiation-sensitive resin constituent may be presented. Moreover, on the occasion of the polymerization in the approach of the above (i) - (iii), molecular weight modifiers, such as a mercaptan compound and a halogen hydrocarbon, can be used if needed.

[0025] although the molecular weight of a polymer (A) can be adjusted by choosing appropriately polymerization conditions, such as a monomer presentation, a radical polymerization initiator, a molecular weight modifier, and polymerization temperature, -- polystyrene equivalent weight average molecular weight (henceforth "Mw") -- it is -- usually -- 5,000-200,000 -- it is 7,000-100,000 preferably. In this case, when there is a possibility that Mw of a polymer (A) may fall and reinforcement may become inadequate [the plating resistance of the resin film] less than by 5,000 and 200,000 is exceeded on the other hand, the alkali solubility after exposure of a polymer falls and there is an inclination for formation of a detailed pattern to become difficult. In this invention, a polymer (A) is independent, or two or more sorts can be mixed and used for it.

[0026] (B) Pori (vinyl low-grade alkyl ether) used for Pori (vinyl low-grade alkyl ether) this invention consists of independent or the polymer obtained by carrying out the polymerization of two or more sorts of mixture (**) of the vinyl low-grade alkyl ether expressed with the following general formula (2).

[0027]



In [general formula (2), R3 shows the alkyl group of the shape of a straight chain of carbon numbers 1-5, and the letter of branching.]

[0028] In a general formula (2), a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, i-butyl, n-pentyl radical, i-pentyl radical, etc. can be mentioned, for example as an alkyl group of the shape of a straight chain of carbon numbers 1-5, and the letter of branching. A methyl group, an ethyl group, and i-butyl are desirable among these alkyl groups, and especially a methyl group is desirable. In this invention, especially desirable Pori (vinyl low-grade alkyl ether) is Pori (vinyl methyl ether).

[0029] The polymerization of vinyl low-grade alkyl ether can be carried out with a conventional method under existence of a cationic polymerization catalyst and in a suitable solvent. As said cationic polymerization catalyst, for example A sulfuric acid, a hydrochloric acid, a hydrobromic acid, Proton acid, such as phosphoric acid, a chlorosulfonic acid, trifluoroacetic acid, and p-toluenesulfonic acid; An aluminum chloride, Acid halogenation metals, such as aluminium bromide, ****-ized boron, a titanium tetrachloride, and a tin tetrachloride Mixture of these acid halogenation metals and cocatalysts, such as water, alcohol, hydrogen halide, and alkyl halide; Triethylaluminum, Mixture with the cocatalyst of organometallic compounds, such as triisobutylaluminum, diethyl chloro aluminum, and ethyl dichloro aluminum, the these organometallic compounds, water, the ether, etc., etc. can be mentioned. These cationic polymerization catalysts are independent, or two or more sorts can be mixed and used for them. Moreover, it is stable under cationic polymerization conditions among the solvents illustrated about the solution polymerization method for manufacturing a polymer (A) as said solvent, for example, or the solvent which can also turn into cocatalyst of cationic polymerization can be mentioned.

[0030] Mw(s) of Pori (vinyl low-grade alkyl ether) are 10,000-100,000 preferably [it is desirable and] to 1,000-200,000, and a pan. Pori (vinyl low-grade alkyl ether) has what [from] has a fluidity at a room temperature to the thing of the shape of flexible resin with the polymerization degree, and these are used, choosing them suitably.

[0031] this invention -- setting -- Pori (vinyl low-grade alkyl ether) -- independent -- or two or more sorts can be mixed and used. the time of the amount of the Pori (vinyl low-grade alkyl ether) used making the sum total of a polymer (A) and Pori (vinyl low-grade alkyl ether) the 100 weight sections -- desirable -- 5 - 60 weight section -- it is 10 - 50 weight section still more preferably. In this case, when a crack may occur in the resist pattern used as mold in rinsing / desiccation process after plating at the time of the amount of the Pori (vinyl low-grade alkyl ether) used manufacturing the plating molding object of a thick film under in 5 weight sections and 60 weight sections are exceeded on the other hand preferably, the contrast of the exposure section and an unexposed part falls at the time of the development for forming a pattern, and there is a possibility that a pattern configuration may be spoiled.

[0032] The radiation-sensitive acid generator (henceforth "an acid generator (C)") used for acid generator (C) this invention Are the compound which generates an acid by exposure and the acid dissociation nature functional group which exists in a polymer (A) according to an operation of this acid dissociates. For example, the exposure section of the resin film which acid functional groups, such as a carboxyl group and a phenolic hydroxyl group, generated, consequently was formed from the positive type radiation-sensitive resin constituent serves as soluble at an alkaline developer, and can form the pattern of a positive type. As an acid generator (C), an onium salt compound (however, a thio FENTIUMU salt compound is included.), a halogen content compound, a diazoketone compound, a sulfone compound, a sulfonic-acid compound, a sulfone imide compound, a diazomethane compound, etc. can be mentioned, for example. Hereafter, the example of these compounds is shown.

[0033] As an onium salt compound onium salt compound, iodonium salt, sulfonium salt, phosphonium salt, diazonium salt, pyridinium salt, etc. can be mentioned, for example. As an example of a desirable onium salt compound Diphenyliodonium trifluoromethane sulfonate, diphenyliodonium p-toluene sulfonate, Diphenyliodonium hexafluoroantimonate, diphenyliodonium hexafluorophosphate, Diphenyliodonium tetrafluoroborate, triphenylsulfonium trifluoromethane sulfonate, Triphenyl hexafluoroantimonate, triphenylsulfonium hexafluorophosphate, 4-t-buthylphenyl diphenyl sulfonium trifluoromethane sulfonate, 4-t-buthylphenyl diphenyl sulfonium perfluoro-n-octane sulfonate, 4-t-buthylphenyl diphenyl sulfonium pyrene sulfonate, 4-t-buthylphenyl diphenyl sulfonium n-dodecylbenzene sulfonate, 4-t-buthylphenyl diphenyl sulfonium p-toluene sulfonate, 4-t-buthylphenyl diphenyl sulfonium benzene sulfonate, 4, and 7-G n-butoxy naphthyl tetrahydro CHIOFENIUMUTORIFURUORO methanesulfonate etc. can be mentioned.

[0034] As a halogen content compound halogen content compound, a halo alkyl group content hydrocarbon compound,

a halo alkyl group content heterocyclic compound, etc. can be mentioned, for example. As an example of a desirable halogen content compound 1, 10-dibromo-n-Deccan, 1, and 1-screw (4-chlorophenyl) - 2, 2, and 2-trichloroethane, Phenyl-bis(TORIKURORO methyl)-s-triazine, 4-methoxyphenyl-bis(TORIKURORO methyl)-s-triazine, (TORIKURORO methyl)-s-triazine derivatives, such as styryl-bis(TORIKURORO methyl)-s-triazine and naphthyl-bis(TORIKURORO methyl)-s-triazine, etc. can be mentioned.

As a diazoketone compound diazoketone compound, 1, a 3-diketo-2-diazo compound, a diazo benzoquinone compound, a diazo naphthoquinone compound, etc. can be mentioned, for example. As an example of a desirable diazoketone compound, a 1 of 1 of phenols, 2-naphthoquinonediazide-4-sulfonate ghost, and phenols and 2-naphthoquinonediazide-5-sulfonate ghost etc. can be mentioned.

As a sulfone compound sulfonation object, a beta-keto sulfone, beta-sulfonyl sulfone, alpha-diazo compound of these compounds, etc. can be mentioned, for example. As an example of a desirable sulfone compound, 4-tris phenacyl sulfone, a mesityl phenacyl sulfone, bis(phenyl sulfonyl) methane, etc. can be mentioned.

As a sulfonic-acid compound sulfonic-acid compound, an alkyl sulfonate, a halo alkyl sulfonate, an aryl sulfonate, imino sulfonate, etc. can be mentioned, for example. As an example of a desirable sulfonic-acid compound, benzoin tosylate, pyrogallol tris trifluoromethane sulfonate, o-nitrobenzyl trifluoromethane sulfonate, o-nitrobenzyl-p-toluene sulfonate, etc. can be mentioned.

[0035] a sulfone imide compound -- as an example of a desirable sulfone imide compound N-(trifluoromethyl sulfonyloxy)succinimide, N-(trifluoromethyl sulfonyloxy)phthalimide, N-(trifluoromethyl sulfonyloxy) diphenyl maleimide, The N-(trifluoromethyl sulfonyloxy) bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(trifluoromethyl sulfonyloxy)-7-OKISA bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(trifluoromethyl sulfonyloxy) bicyclo [2.2.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(trifluoromethyl sulfonyloxy) naphthyl imide, N-(4-methylphenyl sulfonyloxy) succinimide, N-(4-methylphenyl sulfonyloxy) phthalimide, N-(4-methylphenyl sulfonyloxy) diphenyl maleimide, The N-(4-methylphenyl sulfonyloxy) bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(4-methylphenyl sulfonyloxy)-7-OKISA bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(4-methylphenyl sulfonyloxy) bicyclo [2.2.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(4-methylphenyl sulfonyloxy) naphthyl imide, [0036] N-(2-trifluoromethyl phenylsulfonyloxy) succinimide, N-(2-trifluoromethyl phenylsulfonyloxy) phthalimide, N-(2-trifluoromethyl phenylsulfonyloxy) diphenyl maleimide, The N-(2-trifluoromethyl phenylsulfonyloxy) bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(2-trifluoromethyl phenylsulfonyloxy)-7-OKISA bicyclo [2.2.1] hept-5-en -2, 3-dicarboxyimide, The N-(2-trifluoromethyl phenylsulfonyloxy) bicyclo [2.2.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(2-trifluoromethyl phenylsulfonyloxy) naphthyl imide, N-(4-fluoro phenylsulfonyloxy) succinimide, the N-(4-fluoro phenylsulfonyloxy)-7-OKISA bicyclo [2.1.1] hept-5-en -2, 3-dicarboxyimide, The N-(4-fluoro phenylsulfonyloxy) bicyclo [2.1.1] heptane -5, 6-oxy-- 2, 3-dicarboxyimide, N-(4-fluoro phenylsulfonyloxy) naphthyl imide, N-(10-camphor sulfonyloxy) naphthyl imide, etc. can be mentioned.

[0037] a diazomethane compound -- as an example of a desirable diazomethane compound, bis (trifluoromethylsulfonyl) diazomethane, bis(cyclohexyl sulfonyl) diazomethane, bis(phenyl sulfonyl) diazomethane, bis (p-tosyl) diazomethane, methyl sulfonyl-p-tosyl diazomethane, the cyclohexyl sulfonyl -1, 1-dimethyl ethyl sulfonyl diazomethane, bis(1 and 1-dimethyl ethyl sulfonyl) diazomethane, etc. can be mentioned.

[0038] Among these acid generators (C), still more preferably 4-t-buthylphenyl diphenyl sulfonium trifluoromethane sulfonate, 4-t-buthylphenyl diphenyl sulfonium perfluoro-n-octane sulfonate, 4-t-buthylphenyl diphenyl sulfonium pyrene sulfonate, It is 4 and 7-G n-butoxy naphthyl tetrahydro CHIOFENIUMUTORIFURUORO methanesulfonate etc. Especially, it is 4-t-buthylphenyl diphenyl sulfonium trifluoromethane sulfonate, 4, and 7-G n-butoxy naphthyl tetrahydro CHIOFENIUMUTORIFURUORO methanesulfonate etc. In this invention, an acid generator (C) is independent, or two or more sorts can be mixed and used for it.

[0039] the time of the amount of the acid generator (C) used making the sum total of a polymer (A) and Pori (vinyl low-grade alkyl ether) the 100 weight sections from a viewpoint which secures the sensibility as a resist, definition, a pattern configuration, etc. -- usually -- 0.1 - 20 weight section -- it is 0.3 - 10 weight section preferably. In this case, when there is an inclination for sensibility and definition to fall [the amount of the acid generator (C) used] under in the 0.1 weight section and 20 weight sections are exceeded on the other hand, the transparency over a radiation falls and there is an inclination for a pattern configuration to deteriorate.

[0040] It is desirable to blend with the positive type radiation-sensitive resin constituent of acid diffusion control agent this invention the acid diffusion control agent which has the operation which controls the diffusion in the resin film of

the acid generated from an acid generator (C), and controls the chemical reaction in an unexposed part which is not desirable. While the storage stability of a constituent improves and the resolution as a resist improves further by using such an acid diffusion control agent, line breadth change of the pattern by fluctuation of the length soaking time from exposure to PEB can be suppressed, and it becomes what was extremely excellent in process stability. The nitrogen-containing organic compound from which basicity does not change with the exposure or heating of a plating molding object in a production process as an acid diffusion control agent is desirable.

[0041] As said nitrogen-containing organic compound, for example n-hexylamine, n-heptyl amine, n-octyl amine, n-nonyl amine, ethylenediamine, N and N, N', N'-tetramethylethylenediamine, Tetramethylenediamine, hexamethylenediamine, 4, and 4'-diamino diphenylmethane, A - diamino diphenyl ether, and 4 and 4' 4, 4'-diamino benzophenone, A 4 and 4'-diamino diphenylamine, a formamide, N-methyl formamide, N,N-dimethylformamide, an acetamide, N-methyl acetamide, N,N-dimethylacetamide, a propione amide, a benzamide, Pyrrolidone, N-methyl pyrrolidone, methyl urea, 1, and 1-dimethylurea, 1, 3-dimethylurea, 1, 1 and 3, 3-tetramethyl urea, 1, 3-diphenyl urea, An imidazole, benzimidazole 4-methyl imidazole, 8-oxyquinoline, Acridine, pudding, pyrrolidine, piperidine, 2 and 4, 6-Tori (2-pyridyl)-S-triazine, morpholine, 4-methyl morpholine, piperazine, 1, 4-dimethyl piperazine, 1, and 4-diazabicyclo [2.2.2] octane etc. can be mentioned. 2, 4, and 6-Tori (2-pyridyl)-s-triazine is desirable especially among these nitrogen-containing organic compounds. Said acid diffusion control agent is independent, or can mix and use two or more sorts.

[0042] the time of the amount of the acid diffusion control agent used making the sum total of a polymer (A) and Pori (vinyl low-grade alkyl ether) the 100 weight sections -- usually -- below 15 weight sections -- desirable -- 0.001 - 10 weight section -- it is 0.005 - 5 weight section still more preferably. In this case, when the amount of the acid diffusion control agent used exceeds 15 weight sections, there is an inclination for the development nature of the sensibility as a resist or the exposure section to fall. In addition, there is a possibility that the pattern configuration and dimension fidelity as a resist may fall that the amount of the acid diffusion control agent used is under the 0.001 weight section depending on process conditions.

[0043] to other alkali fusibility resin and the positive type radiation-sensitive resin constituent of this invention, a polymer (A) and alkali fusibility resin (the following -- "-- others -- it is called alkali fusibility resin".) other than Pori (vinyl low-grade alkyl ether) can be added by the case. Other alkali fusibility resin is resin meltable to an alkaline developer which has one or more sorts of acid functional groups, such as the functional group which shows an alkali developer and compatibility, for example, a phenolic hydroxyl group, and a carboxyl group. As a result of control of the dissolution rate to the alkaline developer of the resin film formed from the positive type radiation-sensitive resin constituent by adding such alkali fusibility resin becoming easier, development nature can be raised further.

[0044] Although it is not limited especially as long as other alkali fusibility resin is meltable to an alkaline developer, as other desirable alkali fusibility resin For example, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, p-isopropenyl phenol, p-vinyl benzoic acid, p-carboxy methyl styrene, p-carboxy methoxy styrene, an acrylic acid, a methacrylic acid, a crotonic acid, A maleic acid, a fumaric acid, an itaconic acid, citraconic acid Mesaconic acid, The addition polymerization system resin containing the repeating unit to which the polymerization nature unsaturated bond of at least one sort of monomers which have acid functional groups, such as a cinnamic acid, cleft, the polycondensation system resin containing the condensed system repeating unit which has the acid functional group represented by novolak resin, etc. can be mentioned. Although the addition polymerization system resin of alkali fusibility may consist of only repeating units to which the polymerization nature unsaturated bond of the monomer which has said acid functional group cleft, as long as the generated resin is meltable to an alkali developer, it can also contain further one or more sorts of other repeating units.

[0045] As a repeating unit besides the above, for example Styrene, alpha methyl styrene, o-vinyltoluene, m-vinyltoluene, p-vinyltoluene, a maleic anhydride, Acrylonitrile, a methacrylonitrile, croton nitril, mallein nitril, Fumaronitrile, mesa KONNITORIRU, SHITORAKONNITORIRU, ITAKON nitril, Acrylamide, methacrylamide, a croton amide, a mallein amide, A fumaric amide, mesa KONAMIDO, SHITORAKONAMIDO, an ITAKON amide, The unit in which polymerization nature unsaturated bonds, such as 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, N-vinyl aniline, N-vinyl-epsilon caprolactam, N-vinyl pyrrolidone, and N-vinyl imidazole, cleft can be mentioned.

[0046] As addition polymerization system resin of alkali fusibility, the permeability of the radiation when considering as the resin film is high, and the copolymer of Pori (p-hydroxystyrene) and p-isopropenyl phenol etc. is desirable especially from a viewpoint of excelling also in dry etching resistance. Mw of the addition polymerization system resin

of alkali fusibility -- usually -- 1,000-200,000 -- it is 5,000-50,000 preferably.

[0047] Moreover, although the polycondensation system resin of alkali fusibility may consist of only condensed system repeating units which have an acid functional group, as long as the generated resin is meltable to an alkali developer, it can also contain other condensed system repeating units further. Such polycondensation system resin can be manufactured by carrying out the polycondensation (**) of one or more sorts of phenols, and one or more sorts of aldehydes under existence of an acid catalyst or a basic catalyst and in a water medium or the mixed medium of water and a hydrophilic solvent with the polycondensation component which can form other condensed system repeating units by the case. As said phenols, for example o-cresol, m-cresol, P-cresol, 2, 3-xyleneol, 2, 4-xyleneol, 2, 5-xyleneol, 3, 4-xyleneol, 3,5-xyleneol, 2 and 3, a 5-trimethyl phenol, 3 and 4, a 5-trimethyl phenol, etc. can be mentioned. As said aldehydes For example, formaldehyde, a trioxane, a paraformaldehyde, a benzaldehyde, an acetaldehyde, a propyl aldehyde, phenylacetaldehyde, etc. can be mentioned. Mw of the polycondensation system resin of alkali fusibility -- usually -- 1,000-100,000 -- it is 2,000-50,000 preferably. Other alkali fusibility resin of these is independent, or two or more sorts can be mixed and used for it. The amount of other alkali fusibility resin used is usually below the 200 weight sections, when the sum total of a polymer (A) and Pori (vinyl low-grade alkyl ether) is made into the 100 weight sections.

[0048] The surface active agent which shows the operation which improves spreading nature, development nature, etc. to a surface active agent and the positive type radiation-sensitive resin constituent of this invention can be added. As said surface active agent, the polyoxyethylene lauryl ether, polyoxyethylene stearylether, the polyoxyethylene oleyl ether, the polyoxyethylene n-octyl phenol ether, the polyoxyethylene n-nonyl phenol ether, a polyethylene-glycol JIRAU rate, polyethylene-glycol distearate, etc. can be mentioned, for example. These surfactants are independent, or two or more sorts can be mixed and used for them. The amount of the surface active agent used is usually below 2 weight sections, when the sum total of a polymer (A) and Pori (vinyl low-grade alkyl ether) is made into the 100 weight sections.

[0049] The thermal polymerization inhibitor for raising an ultraviolet ray absorbent, a sensitizer, a dispersant, a plasticizer, and preservation stability, for example as other additives which can be blended with the positive type radiation-sensitive resin constituent of this invention, an antioxidant, etc. can be mentioned to other additive pans, and especially, since there is an operation which prevents the photoreaction by the surroundings lump by the unexposed part of the scattered light at the time of exposure, the ultraviolet ray absorbent is useful. The compound which has an absorbancy index high as such an ultraviolet ray absorbent in the wavelength region of the ultraviolet rays used for exposure is desirable. Moreover, an organic pigment can also be used for the same purpose.

[0050] (D) Dimethyl sulfoxide besides the solvent illustrated about the solution polymerization method for manufacturing said polymer (A) as an organic solvent used for organic solvent this invention, for example, acetonylacetone, an isophorone, propylene carbonate, etc. can be mentioned. These organic solvents are independent, or two or more sorts can be mixed and used for them. the time of making the sum total of a polymer (A) and Pori (vinyl low-grade alkyl ether) into the 100 weight sections, although it was not limited especially when the amount of the organic solvent used can be adjusted in consideration of the method of application of a positive type radiation-sensitive resin constituent, the application of the plating molding object manufactured, etc. and homogeneity could be made to mix a constituent -- desirable -- the 20 - 400 weight section -- it is the 50 - 300 weight section still more preferably.

[0051] The positive type radiation-sensitive resin constituent of this invention can be used especially suitable for manufacture of plating molding objects, such as a bump of an integrated circuit device, or wiring. Moreover, after applying on a base material film and drying, by exfoliating this base material film, the positive type radiation-sensitive resin constituent of this invention can be used as the resin film, and this positive type radiation-sensitive resin film can be used for it suitable for manufacture of the same plating molding object as the above. In this case, as an approach of applying a positive type radiation-sensitive resin constituent on a base material film, a spin coat method, the roll coat method, screen-stencil, the applicator method, etc. can be mentioned, for example. In addition, especially the ingredient of a base material film is not limited, and a proper thing can be used for it as long as it has necessary reinforcement.

[0052] Hereafter, the manufacture approach of the plating molding object of this invention is explained. The manufacture approach (henceforth "the manufacture approach (1)") of the plating molding object using the positive type radiation-sensitive resin constituent in this invention The process which dries it after applying a (b) positive type radiation-sensitive resin constituent on the substrate which has a conductive layer on a front face, and forms the resin film, The process which carries out exposure afterbaking to the (b) this resin film at a predetermined configuration,

develops negatives further, and forms a pattern, (Ha) It consists of passing through the process which uses as mold this pattern formed on the substrate, carries out electrolytic plating to predetermined thickness, and forms a plating molding object, the process which exfoliates a (d) substrate to a resin film part, and the process which removes conductive layers other than the field in which the plating molding object on a (e) substrate was formed.

[0053] Moreover, the manufacture approach (henceforth "the manufacture approach (2)") of the plating molding object using the positive type radiation-sensitive resin film in this invention The process which carries out the laminating of the (b) positive type radiation-sensitive resin film on the substrate which has a conductive layer on a front face, The process which carries out exposure afterbaking to the resin film by which the (b) laminating was carried out at a predetermined configuration, develops negatives further, and forms a pattern, (Ha) It consists of passing through the process which uses as mold this pattern formed on the substrate, carries out electrolytic plating to predetermined thickness, and forms a plating molding object, the process which exfoliates a (d) substrate to a resin film part, and the process which removes conductive layers other than the field in which the plating molding object on a (e) substrate was formed.

[0054] In the manufacture approach (1) and the manufacture approach (2), soda glass, quartz glass, silicon carbide, titanium carbide, zirconium carbide, boron nitride, aluminum nitride, silicon nitride, silicon, germanium, a gallium arsenide, gallium phosphorus, etc. can be mentioned as a substrate, for example. Moreover, as an electrical conducting material used in order to form a conductive layer on the surface of a substrate, aluminum, copper, silver, gold, palladium, two or more sorts of these alloys (for example, palladium-gold), etc. can be mentioned, for example. The conductive layer on the front face of a substrate can be formed from processing said electrical conducting material by the spatter. Although especially the thickness of a conductive layer is not limited, it is usually about 500-2,000Å preferably 200-10,000Å.

[0055] In the manufacture approach (1), a spin coat method, the roll coat method, screen-stencil, the applicator method, etc. can be mentioned, for example as an approach of applying a positive type radiation-sensitive resin constituent on a substrate. Moreover, in the manufacture approach (2), the pasting-up method, the rolling method, the pressing method, etc. can be mentioned, for example as an approach of carrying out the laminating of the positive type radiation-sensitive resin film on a substrate. the thickness of the resin film in the manufacture approach (1) and the manufacture approach (2) -- the application of a plating molding object -- changing -- for example, a bump's case -- usually -- 20-100 micrometers -- desirable -- 20-80 micrometers -- further -- desirable -- 20-50 micrometers -- it is -- moreover, the case of wiring -- usually -- 3-30-micrometer 1-30 micrometers are 5-20 micrometers still more preferably preferably.

[0056] The radiation which can mention X-rays, such as charged-particle lines, such as an electron ray besides the far ultraviolet rays represented from a low pressure mercury lamp, a high pressure mercury vapor lamp, an ultrahigh pressure mercury lamp, a metal halide lamp, g line stepper, i line stepper, etc. to an ultraviolet-rays;KrF excimer laser or an ArF excimer laser etc., and a synchrotron radiation line, etc. as a radiation used for exposure, and is in within the limits whose wavelength is 150-500 micrometers above all is desirable. In the case of the ultraviolet rays from a high pressure mercury vapor lamp, light exposure is usually 1,000 - 20,000 J/m², for example, although it changes with the class of radiation, the presentation of a constituent, thickness of the resin film, etc. It is extent. After exposure performs PEB in order to promote dissociation of the acid dissociation nature functional group in a polymer (A). Although the processing condition changes with the presentation of a constituent, thickness of the resin film, etc., 70-120 degrees C, it is 100-120 degrees C preferably, and is usually 30 seconds - about 10 minutes.

[0057] Then, the pattern of a predetermined configuration is formed by developing negatives with an alkaline developer, and dissolving and removing the exposure section. As a developing-negatives method, the shower developing-negatives method, the spray developing-negatives method, the immersion developing-negatives method, the paddle developing-negatives method, etc. can be mentioned with an alkaline developer, for example. Developing time is usually about 1 - 30 minutes in ordinary temperature. The alkaline water solution which dissolved alkaline compounds, such as a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium silicate, aqueous ammonia, ethylamine, n propylamine, diethylamine, triethylamine, monoethanolamine, diethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, a choline, a pyrrole, and a piperidine, in water as said alkaline developer, for example so that concentration might become 1 - 10% of the weight can be mentioned. Optimum dose addition of organic solvents, surfactants, etc., such as a methanol and ethanol, can also be carried out at said alkaline water solution. In addition, after developing negatives with an alkaline developer, generally it washes with water and dries.

[0058] A plating molding object is formed by carrying out electrolytic plating to predetermined thickness after development by using as mold the pattern formed on the substrate. In order to raise the compatibility of a pattern front face and plating liquid on the occasion of electrolytic plating, it is desirable to carry out [processing / for example, by the oxygen plasma / ashing] hydrophilization processing of the pattern formed from the resin film. As plating liquid used for electrolytic plating, the thing containing the same component as the metal and alloy which were illustrated about said conductive layer can be mentioned, for example. although the conditions of electrolytic plating change with presentations of plating liquid etc. -- the case of for example, gold plate -- temperature -- usually -- 40-70 °C -- desirable -- about 55-70 degrees C -- it is -- current density -- usually -- 0.1 - 1 A/dm² -- desirable -- 0.2 - 0.8 A/dm² It is extent. After rinsing and drying, after plating observes the condition of a pattern, thickness, a condition of a plating molding object, etc., and performs electrolytic plating again if needed.

[0059] the thickness of a plating molding object -- the application -- changing -- for example, a bump's case -- usually - 5-50 micrometers -- desirable -- 10-30 micrometers -- further -- desirable -- 15-25 micrometers -- it is -- moreover, the case of wiring -- usually -- 3-20-micrometer 1-30 micrometers are 5-15 micrometers still more preferably preferably.

[0060] Then, a resin film part is exfoliated from a substrate. As the exfoliation approach of a resin film part, the approach of carrying out grade immersion of the substrate, for example for 1 - 10 minutes etc. can be mentioned to the exfoliation liquid stirred, for example at 20-80 degrees C. As said exfoliation liquid, dimethyl sulfoxide, the mixed solution of N,N-dimethylformamide, etc. can be used, for example. A predetermined plating molding object is obtained after exfoliation of a resin film part by removing conductive layers other than the field in which the plating molding object on a substrate was formed, for example, by the wet etching method etc. Furthermore, the positive type radiation-sensitive resin constituent of this invention and the positive type radiation-sensitive resin film are useful also as the resist for thin films, a platemaking ingredient, a charge of the Mitsunari mold material, etc.

[0061] This invention is not restrained by these examples, although an example is given and the gestalt of operation of this invention is explained more concretely hereafter. They are weight criteria unless the section and % mention specially below.

<Composition of a polymer (A)> Synthetic example 1p-acetoxy styrene 71g, 2-benzyl-2-propylacrylate 23g, and styrene 6g were mixed with dioxane 150g, and it considered as the homogeneity solution. The polymerization of the reaction temperature was maintained and carried out to 70 degrees C for 7 hours, having added azobisisobutyronitrile 4.5g and continuing bubbling by nitrogen gas, after carrying out bubbling of this solution with nitrogen gas for 30 minutes. The reaction solution was mixed with a lot of hexanes after polymerization termination, and the generated polymer was made to solidify. Subsequently, after remelting a polymer to dioxane, the actuation made to solidify by the hexane again was repeated several times, the unreacted monomer was removed, it dried at 50 degrees C under reduced pressure, and the white polymer was obtained. After dissolving the obtained polymer in propylene-glycol-monomethyl-ether 500g, 50g of aqueous ammonia solutions was added 25%, and it hydrolyzed by stirring for 5 hours at 80 degrees C. Subsequently, after throwing in the reaction solution in 0.2% oxalic acid water solution and making a polymer solidify, it rinsed, it dried at 50 degrees C under reduced pressure, and the white polymer was obtained. Mw was 10,000 and the copolymerization weight ratio of p-hydroxystyrene, 2-benzyl-2-propylacrylate, and styrene of this polymer was 70:10:20 the result of ultimate analysis. Let this polymer be a polymer A-1.

[0062] Synthetic example 2p-isopropenyl phenol 35g and 2-benzyl-2-propylacrylate 65g were mixed with dioxane 150g, and it considered as the homogeneity solution. The polymerization of the reaction temperature was maintained and carried out to 70 degrees C for 7 hours, having added azobisisobutyronitrile 4.5g and continuing bubbling by nitrogen gas, after carrying out bubbling of this solution with nitrogen gas for 30 minutes. The reaction solution was mixed with a lot of hexanes after polymerization termination, and the generated polymer was made to solidify. Subsequently, after remelting a polymer to dioxane, the actuation made to solidify by the hexane again was repeated several times, the unreacted monomer was removed, it dried at 50 degrees C under reduced pressure, and the white polymer was obtained. Mw was 16,000 and the copolymerization weight ratio of p-isopropenyl phenol and 2-benzyl-2-propylacrylate of this polymer was 35:65 as a result of ultimate analysis. Let this polymer be a polymer A-2.

[0063] As synthetic example 3 monomer, the white polymer was obtained like the synthetic example 2 except having used p-isopropenyl phenol 30g, 2-benzyl-2-propylacrylate 20g, and isobornyl acrylate 50g. Mw was 19,000 and the copolymerization weight ratio of p-isopropenyl phenol, 2-benzyl-2-propylacrylate, and isobornyl acrylate of this polymer was 30:20:50 as a result of ultimate analysis. Let this polymer be a polymer A-3.

[0064] As synthetic example 4 monomer, the white polymer was obtained like the synthetic example 2 except having used p-isopropenyl phenol 45g, 2-benzyl-2-propylacrylate 35g, and ethyl acrylate 20g. Mw was 15,000 and the copolymerization weight ratio of p-isopropenyl phenol, 2-benzyl-2-propylacrylate, and ethyl acrylate of this polymer was 45:35:20 as a result of ultimate analysis. Let this polymer be a polymer A-4.

[0065] As synthetic example 5 monomer, the white polymer was obtained like the synthetic example 2 except having used p-isopropenyl phenol 40g, 2-benzyl-2-propylacrylate 30g, 2-hydroxypropyl acrylate 10g, and benzyl acrylate 20g. Mw was 16,000 and the copolymerization weight ratio of p-isopropenyl phenol, 2-benzyl-2-propylacrylate, 2-hydroxypropyl acrylate, and benzyl acrylate of this polymer was 40:30:10:20 as a result of ultimate analysis. Let this polymer be a polymer A-5.

[0066] As synthetic example 6 monomer, the white polymer was obtained like the synthetic example 2 except having used p-isopropenyl phenol 37g, 2-benzyl-2-propylacrylate 28g, 2-hydroxypropyl acrylate 5g, and isobornyl acrylate 30g. Mw was 17,000 and the copolymerization weight ratio of p-isopropenyl phenol, 2-benzyl-2-propylacrylate, 2-hydroxypropyl acrylate, and isobornyl acrylate of this polymer was 37:28:5:30 as a result of ultimate analysis. Let this polymer be a polymer A-6.

[0067]

[Example] After mixing each component shown in one to examples 1-10 and example of comparison 2 table 1 and considering as a homogeneity solution, it filtered with the membrane filter made from Teflon (trademark) of 3 micrometers of apertures, and each resin constituent was prepared, in the following way, the patterning substrate and the plating substrate were produced and various evaluations were performed. An evaluation result is shown in Table 2.

[0068] On the silicon wafer substrate with a production diameter [of a golden spatter substrate] of 4 inches, after carrying out sputtering of the chromium so that thickness may become about 500A, on it, sputtering of the gold was carried out so that thickness might become 1,000A, and the conductive layer was formed. Hereafter, the substrate in which this conductive layer was formed is called "golden spatter substrate."

[0069] After using the spin coater for the formation golden spatter substrate of a pattern and applying each resin constituent, on the hot plate, it heated for 5 minutes at 90 degrees C, and the resin film with a thickness of 25 micrometers was formed. Subsequently, through a pattern mask, an ultrahigh pressure mercury lamp (HBO made from OSRAM, output 1,000W) is used, and it is 1,000 - 3,000 J/m². Ultraviolet rays were exposed. Light exposure was checked with the illuminometer (what connected probe UV-35 (electric eye) with UV-M10 (illuminometer) by ORC Manufacturing Co., Ltd.). For [PEB] 5 minutes was performed at 100 degrees C on the hot plate after exposure. subsequently, the stream after being immersed for 1 minute at a room temperature using a tetramethylammonium hydroxide water solution 2.38% of the weight and developing negatives -- the nitrogen blow was washed and carried out and the pattern was formed. Hereafter, the substrate in which this pattern was formed is called "patterning substrate."

[0070] To the formation patterning substrate of a plating molding object, ashing processing (output 200W, the oxygen flow rate of 200ml, processing-time 2 minutes) by the oxygen plasma was performed as pretreatment of electrolytic plating, and hydrophilization processing was performed. Subsequently, this substrate is immersed into 2l. (the N.E. Chemcat Corp. make, trade name ECF88K) of non cyanogen liquid gilding, and they are 60 degrees C and current density 0.5 A/dm² whenever [plating bath temperature]. It set up, electrolytic plating was performed for about 60 minutes, and the plating molding object for bumps with a thickness of 19-20 micrometers was formed. subsequently, a stream -- the substrate which has a plating molding object was obtained by washing, being immersed for 5 minutes at a room temperature into dimethyl sulfoxide and the mixed solution (weight ratio = 50:50) of N.N-dimethylformamide, exfoliating a resin film part, and removing conductive layers other than the field which formed the plating molding object on a substrate further by wet etching, after blowing and drying with nitrogen gas. Hereafter, the substrate which has this plating molding object is called "plating substrate."

[0071] When the pattern (30-micrometer width-of-face omission pattern / 10-micrometer width-of-face remnants pattern) of 40-micrometer pitch was formed in an evaluation (1) sensibility golden spatter substrate with a mask design dimension, light exposure from which it extracts and the dimension of the pars basilaris ossis occipitalis of a pattern is set to 30 micrometers was made into the optimal light exposure, and it evaluated from this optimal light exposure to it. (2) Two patterning substrates which formed separately two sorts of patterns (30-micrometer width-of-face omission pattern / 10-micrometer width-of-face remnants pattern, 32-micrometer width-of-face omission pattern / 8-micrometer width-of-face remnants pattern) of 40-micrometer pitch with the resolution mask design dimension were observed with

the optical microscope and the scanning electron microscope, and the following criteria estimated them.

O : 32-micrometer width-of-face omission pattern / 8-micrometer width-of-face remnants pattern is resolvable.

** : Although 30-micrometer width-of-face omission pattern / 10-micrometer width-of-face remnants pattern is resolvable, 32-micrometer width-of-face omission pattern / 8-micrometer width-of-face remnants pattern is unresolvable.

x: or [that the pattern of 40 micrometer pitch is unresolvable] -- or it is unresolvable with sufficient repeatability.

[0072] (3) Make it be the same as that of formation of said plating molding object to a crack resistance patterning substrate. Wash and the substrate (substrate which has not exfoliated the resin film part) blown and dried with nitrogen gas is left in the clean room held to the room temperature of 23 degrees C, and about 45% of humidity. the stream after forming the plating molding object for bumps -- 3 hours and 24 hours after, the substrate front face was observed with the optical microscope, and the following criteria estimated. Here, a "remnants pattern" is equivalent to a resist pattern.

O : A crack does not generate 24 hours after in a remnants pattern.

** : Although a crack does not occur in a remnants pattern 3 hours after, a crack occurs in a remnants pattern 24 hours after.

x: 3 hours after, a crack occurs in a remnants pattern.

(4) The patterning substrate in which the pattern (30-micrometer width-of-face omission pattern / 10-micrometer width-of-face remnants pattern) of 40-micrometer pitch was formed was observed and extracted with the optical microscope and the scanning electron microscope with the dimension fidelity mask dimension of a pattern, the top dimension (Wt) and pars-basilaris-ossis-occipitalis dimension (Wb) of a pattern were measured, and the dimension fidelity of the pattern to a mask dimension (30 micrometers) was evaluated.

[0073] (5) The plating substrate which formed the plating molding object in the patterning substrate which formed the pattern (30-micrometer width-of-face omission pattern / 10-micrometer width-of-face remnants pattern) of 40-micrometer pitch with the configuration mask dimension of plating was observed with the optical microscope and the scanning electron microscope, and the following criteria estimated it.

O : The configuration of plating is imprinting faithfully the pattern configuration formed from the resin film, and a wen-like protrusion [abnormality] is not accepted.

x: The configuration of plating does not imprint faithfully the pattern configuration formed from the resin film, but a wen-like protrusion [abnormality] is accepted.

(6) The plating substrate which formed the plating molding object in the patterning substrate which formed the pattern (30-micrometer width-of-face omission pattern / 10-micrometer width-of-face remnants pattern) of 40-micrometer pitch with the dimension fidelity mask dimension of plating was observed with the optical microscope and the scanning electron microscope, the top dimension (Wt) and pars-basilaris-ossis-occipitalis dimension (Wb) of a plating part were measured, and the dimension fidelity of plating to a mask dimension (30 micrometers) was evaluated.

[0074] In Table 1, components other than a polymer (A) are as follows.

Pori (vinyl methyl ether)

B-1: Using the rotary evaporator, the solvent permutation was carried out and the methanol solution (Tokyo formation the product made from Industry, 50 % of the weight of concentration) of Pori (vinyl methyl ether) (Mw=50,000) was used for 2-hydroxy ethyl propionate as a solution of 50 % of the weight of concentration.

Acid generator (C)

C-1: 4 and 7-G n-butoxy naphthyl tetrahydro CHIOFENIUMUTORIFURUORO methanesulfonate C-2: 4-t-buthylphenyl diphenyl -- sulfonium trifluoromethane (sulfonate D) organic solvent D-1:ethyl lactate D- 2:propylene-glycol-monomethyl-ether acetate acid diffusion control agent E-1: -- 2, 4, and 6-Tori (2-pyridyl)-s-triazine [0075]

[Table 1]

表 1

	重合体 (A) (部)	ポリ (ビニルメチ ルエーテル) (部)	酸発生剤 (C) (部)	酸拡散制御剤 (部)	有機溶剤 (部)
実施例 1	A-1 (80)	B-1 (20)	C-1 (1)	—	D-1 (150)
実施例 2	A-1 (70)	B-1 (30)	C-1 (1)	—	D-1 (150)
実施例 3	A-1 (80)	B-1 (20)	C-2 (1)	—	D-1 (150)
実施例 4	A-1 (80)	B-1 (20)	C-1 (1)	—	D-2 (150)
実施例 5	A-1 (80)	B-1 (20)	C-1 (1)	E-1 (0.1)	D-1 (150)
実施例 6	A-2 (80)	B-1 (20)	C-1 (1)	—	D-1 (150)
実施例 7	A-3 (80)	B-1 (20)	C-1 (1)	—	D-1 (150)
実施例 8	A-4 (80)	B-1 (20)	C-1 (1)	—	D-1 (150)
実施例 9	A-5 (80)	B-1 (20)	C-1 (1)	—	D-1 (150)
実施例 10	A-6 (80)	B-1 (20)	C-1 (1)	—	D-1 (150)
比較例 1	A-1 (100)	—	C-1 (1)	—	D-1 (150)
比較例 2	A-2 (100)	—	C-1 (1)	—	D-1 (150)

[0076]

[Table 2]

表 2

	感度 (J/m) ²	解像度	パターンの 寸法忠実性 Wt/Wb (μm)	クラック 耐性	メッキの 形状	メッキの 寸法忠実性 Wt/Wb (μm)
実施例 1	2,000	○	30.3/29.5	○	○	30.7/30.2
実施例 2	2,000	○	31.3/29.2	○	○	31.8/29.8
実施例 3	2,000	○	31.1/29.3	○	○	31.3/29.9
実施例 4	2,000	○	31.6/29.4	○	○	31.9/30.1
実施例 5	3,000	○	30.2/29.7	○	○	30.8/30.4
実施例 6	1,000	○	30.5/29.7	○	○	30.9/30.3
実施例 7	5,000	○	32.0/29.2	○	○	32.5/29.9
実施例 8	2,000	○	31.1/29.5	○	○	32.5/30.7
実施例 9	2,000	○	30.3/29.1	○	○	32.1/29.8
実施例 10	5,000	○	31.4/29.8	○	○	32.0/30.4
比較例 1	2,000	○	30.3/29.7	×	○	30.5/30.0
比較例 2	2,000	○	31.0/29.4	×	○	31.2/29.8

[0077]

[Effect of the Invention] The positive type radiation-sensitive resin constituent of this invention imprints the configuration of the pattern used as mold faithfully also in an electrolytic plating phase, and can form a plating molding object faithful to a mask dimension while it can form the pattern used as the mold of electrolytic plating in a mask dimension faithfully. And the positive type radiation-sensitive resin constituent of this invention does not produce a crack in a resist pattern by rinsing and desiccation under plating and after plating, and is excellent in sensibility, resolution, etc. Therefore, the positive type radiation-sensitive resin constituent of this invention can be used very suitable for manufacture of the plating molding object of thick films, such as a bump or wiring in an integrated circuit device.

[Translation done.]